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**CLINOPTILOLITE-RICH ROCKS IN AGRICULTURAL USE FOR SOIL AMENDMENT
AND POTENTIAL NITROGEN-POLLUTION MITIGATION**

by

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CONTENTS

	Page
Abstract.....	1
Introduction.....	2
Clinoptilolite-rich rocks and their cation-exchange properties.....	3
Occurrences of calcium plus potassium-rich clinoptilolite-rich rocks in the Western U.S.....	4
Rationale for laboratory investigations.....	5
Laboratory methods.....	6
Results of serial exchanges.....	6
Review of cation-exchange results.....	10
Influence of clinoptilolite-rich rocks on pH of water.....	11
Clinoptilolite-rich rocks reactions with liquid commercial ammonium fertilizer.....	12
Cation competition between H^+ versus common soil cations.....	18
Summary.....	19
References cited.....	19

ILLUSTRATIONS

Figure 1. Relations of solution pH for clinoptilolite-rich rocks for exchange AB, 25 percent NaCl.....	21
Figure 2. Relations of solution pH for clinoptilolite-rich rocks for exchange AC, acetic acid of pH = 2.8.....	22
Figure 3. Relations of solution pH for clinoptilolite-rich rocks for exchange AE, 24 percent NH_4Cl	23
Figure 4. Relations of solution pH for clinoptilolite-rich rocks for exchange BC, 25 percent NaCl.....	24
Figure 5. Relations of solution pH for clinoptilolite-rich rocks for exchange BD, acetic acid of pH = 2.8.....	25
Figure 6. Relations of solution pH for clinoptilolite-rich rocks for exchange BG, 40 percent $CaCl_2$	26
Figure 7. Relations of solution pH for clinoptilolite-rich rocks for exchange B1, 25 percent NaCl.....	27
Figure 8. Relations of solution pH for clinoptilolite-rich rocks for exchange BH, acetic acid of pH = 2.8.....	28

Figure 9. Relations of solution pH for clinoptilolite-rich rocks for exchange B2, 25 percent NaCl.....	29
Figure 10. Relations of solution pH for clinoptilolite-rich rocks for exchange CA, 25 percent NaCl.....	30
Figure 11. Relations of solution pH for clinoptilolite-rich rocks for exchange CB, acetic acid of pH = 2.8.....	31
Figure 12. Relations of solution pH of 57.1 weight percent ammonium nitrate after immersion of clinoptilolite-rich rocks for 48 hours.....	32

TABLES

Table 1. Concentrations of certain elements in raw clinoptilolite-rich rocks from the Western U.S. that have high concentrations of calcium plus potassium.....	4
Table 2. Dilutant minerals in raw clinoptilolite-rich rocks from the western U.S. that have high concentrations of calcium plus potassium.....	5
Table 3. Amounts of potassium and calcium in clinoptilolite-rich rocks after 24 percent ammonium chloride exchange (AE), and amounts lost (-) due to exchange.....	7
Table 4. Amounts of potassium and calcium in clinoptilolite-rich rocks after 40 percent calcium chloride exchange (BG), and the amounts of calcium gained and the amounts of potassium lost (-).....	8
Table 5. Amounts of potassium and calcium in clinoptilolite-rich rocks, and the amounts of potassium and calcium lost (-) after acetic acid exchange BH.....	9
Table 6. Amounts of potassium and calcium in clinoptilolite-rich rocks, and the amounts of potassium gained and amounts of calcium lost (-) after the 24 percent potassium chloride exchange (B2A).....	9
Table 7. Amounts of potassium and calcium in clinoptilolite-rich rocks after acetic acid (pH = 2.8) exchange (CB), and the amounts of potassium and calcium lost (-) due to exchange.....	10
Table 8. Relative maximum amounts of potassium and calcium exchange capacities determined in the present study.....	11

	Page
Table 9. Initial and final pH of tap water exposed to clinoptilolite-rich rocks for 21 days.....	11
Table 10. Initial and final pH of tap water exposed to clinoptilolite-rich rocks for 10 days.....	12
Table 11. Concentrations of nitrogen, potassium, and calcium in ammonium polyphosphate-exchanged clinoptilolite-rich rocks.....	13
Table 12. Losses of water-soluble salts from ammonium polyphosphate-exchanged clinoptilolite-rich rocks exposed to near-neutral water.....	13
Table 13. Concentrations of Na, Mg, K, Ca, and N in clinoptilolite-rich rocks exposed to 1:3 diluted 10-34-0 ammonium polyphosphate liquid for 48 hours.....	14
Table 14. Concentrations of Na, Mg, K, Ca, and N in spent liquids after exchange of clinoptilolite-rich rocks in 1:3 diluted 10-34-0 ammonium polyphosphate liquid for 48 hours.....	15
Table 15. Amounts of nitrogen exchanged into clinoptilolite-rich rocks, and amounts of non-exchanged or water soluble nitrogen in clinoptilolite-rich rocks after exposure to 1:3 diluted 10-34-0 ammonium polyphosphate liquid for 48 hours.....	15
Table 16. Concentrations of Na, Mg, K, Ca, and N in clinoptilolite-rich rocks exposed to 57.1 weight percent of ammonium nitrate (AN20) for 48 hours. Weight gains are also given.....	16
Table 17. Concentrations of Na, Mg, K, and Ca in spent liquids after exchange of clinoptilolite-rich rocks in 57.1 weight percent of ammonium nitrate (AN20) for 48 hours.....	17
Table 18. Amounts of nitrogen exchanged into clinoptilolite-rich rocks, and amounts of non-exchanged or water soluble nitrogen in clinoptilolite-rich rocks after exposure to 57.1 weight percent of ammonium nitrate (AN20) for 48 hours.....	17
Table 19. Initial and final pH of cation-rich acidic solutions to which clinoptilolite-rich rocks were exposed CRR: solution = 1:8 and exposure periods are given.....	18

ABSTRACT

Chemical and physical laboratory investigations of clinoptilolite-rich rocks (CRRs) from six deposits in the western U.S. were done to evaluate their potential use for agricultural amendments as carriers of plant nutrients essential for fertilizer applications. CRRs with 4.5 or more weight percent of Ca + K were selected for this study; this was done because high Na CRRs may adversely affect plant growth by cation exchange of large amounts of Na.

These CRRs were exposed to exchange solutions with high concentrations of Na^+ , NH_4^+ , Ca^{2+} , and K^+ salts and low concentrations of H^+ in acetic acid solutions. This was done to establish their cation affinities and their respective competition with H^+ . Serial and multiple exchanges of these cations were done alternately with dilute acetic acid solutions in order to identify cation affinities of the common soil cations versus H^+ . Significant differences were observed among the CRRs.

Exposure of each raw CRR to near-neutral pH water showed that one of them decreases the pH significantly, whereas the others do not.

The CRRs were each placed in two different preparations of commercial liquid N fertilizer solutions to evaluate their capacity to hold N, both as NH_4^+ captured by ion exchange, and as N in soluble forms of ammonium and nitrate salts contained in intracrystalline voids or pore space in 2-4.7 mm-sized CRR granules. Differences in the amounts of NH_4^+ ion-exchanged into the CRRs varied from 250 to 270 percent among the CRRs in two side-by-side tests of six CRRs. Differences in the amounts of total N in the CRRs exposed to the two N-rich solutions varied from 30 to 174 percent among the CRRs. The amounts of total N in dried CRRs after exposure to 57.1 weight percent ammonium nitrate solutions ranged from 4.7 to 8.2 weight percent, or from 94 to 164 pounds of N per ton of CRR. During the exchange of NH_4^+ from the N-rich liquids into the CRRs, plant nutrients such as K and Ca are exchanged out of the crystal structure of clinoptilolites. After drying the CRRs, small amounts of these plant nutrients are available as soluble salts in the pore space of the CRRs.

These investigations were done to assess the potential of Ca- and K-rich CRRs for agricultural applications in which CRR is exposed to N-rich liquids to sequester N and other plant nutrients for slow release when amended CRR is used as fertilizer. The principal reason for examining a slow-nutrient release for plants is that the highly-soluble commercial fertilizers used in current practice are responsible for non-point N pollution of surface and groundwater in many areas of western and central U.S.

The use of amended CRR as fertilizer will also permanently enhance the cation-exchange capacity of the soils to which they are applied. In this regard, the CRR placed in the soil should preferentially, but temporarily extract NH_4^+ by cation exchange when highly soluble commercial NH_4^+ -rich fertilizers are subsequently

applied to the crop fields. The development of plant-nutrient amended CRR and field tests of their economic efficacy as fertilizer carrier are essential.

INTRODUCTION

Nitrogen pollution of groundwater in areas using highly soluble commercial fertilizers has been widely recognized in the U.S. in the past two decades. A recent report by Puckett (1994) shows that agricultural nonpoint sources of nitrogen account for at least 84 percent of the total nitrogen added to the environment; this is due to both commercial fertilizer and animal manure contributions. The midwestern U. S. is most severely impacted, but other areas are also affected (Puckett, 1994, figs. 1 and 2). Nitrogen pollution from commercial fertilizer occurs chiefly in highly permeable (sandy) soils, and in areas with high application rates of fertilizer for high-value crops; however, even clayey soils in the midwestern U.S. exposed to high N-application rates for decades may have a significant impact on groundwater pollution by nitrate. Loss of ammonium nitrogen is partly due to downward mobilization or leaching of N beyond the root zone where it is no longer available to plants; another loss is from denitrification. If ammonium provided by the soluble commercial fertilizer could be temporarily sequestered by cation exchange into clinoptilolite, it may be protected there from bacterial and oxidative degradation to nitrate (NO_3^-) and denitrification, but NH_4^+ will remain available for plant uptake in the root zone (Mumpton and Fishman, 1977). This temporary sequestration of NH_4^+ has two immediate advantages; clinoptilolite-rich rock (CRR) reduces the amount of commercial N fertilizer applied for plant growth (Barbarick and Pirela, 1985), and it decreases nitrogen pollution of groundwater and surface water. CRR also permanently increases the cation-exchange capacity of soils which is desirable. A long-term benefit is that CRR in soil is available during subsequent years to repeatedly perform the same NH_4^+ cation-exchange reactions when ammonium-rich commercial fertilizer is applied to croplands, lawns, golf courses, floriculture, horticulture or similar applications.

Studies of creeping bentgrass using CRR amendment to sand show an increase in clipping yield and fertilizer N recovery by the plants (Ferguson and others, 1986) and a similar study showed a quicker establishment rate of the grass using CRR amendment with sand (Nus and Brauen, 1991). In a recent quantitative study Huang and Petrovic (1994) demonstrated N fertilizer $[(\text{NH}_4)_2\text{SO}_4]$ use efficiency by bentgrass was improved by 16 to 22 % with the addition of CRR to sand in a ratio of CRR:sand = 1:9. Also, water availability using CRR plus sand was almost two times greater than the sand only (Huang and Petrovic; 1994, table 1). These investigations were all oriented to improvement of putting greens on golf courses where commercial fertilizer is used at high application rates and may be applied as often as seven times per year.

CLINOPTILOLITE-RICH ROCKS AND THEIR CATION-EXCHANGE PROPERTIES

Natural occurrences of the zeolite mineral, clinoptilolite, provide a resource of unique cation-exchange properties that can be beneficial in practical uses. For agricultural applications, raw clinoptilolite-rich rocks (CRRs) should have low concentrations of exchangeable sodium, and high concentrations of exchangeable calcium and potassium. High concentrations of exchangeable sodium in CRRs are deleterious to plants of agronomic interest for human and animal nutrition (Nishita and others, 1968; Nishita and Haug, 1972). CRR with relatively high concentrations of calcium plus potassium (e.g. 4.5 weight per cent or more) would be most useful in agricultural applications. However, the amounts of Ca and K (and other cations) determined to be in CRRs by chemical analysis does not necessarily represent exchangeable Ca and K because these cations may also occur in other associated minerals such as feldspars, clay minerals, micas, calcite, and gypsum (Sheppard and Gude, 1982). Except for clay minerals, cations in these dilutant minerals are generally not exchangeable. However, Ca in calcite, and Ca and S in gypsum, though not exchangeable, are available plant nutrients; gypsum is also used as a soil amendment to reduce sodium concentrations in alkaline soils.

When NH_4^+ is captured by raw clinoptilolite, other cation(s) are exchanged from clinoptilolite, in order to maintain charge balance. These exchanged cations include Mg, Na, K, Ca, and minor or trace amounts of Fe, Sr, or Ba. It is most likely that either Na or Ca, or both, are the major cations released from raw clinoptilolite during NH_4^+ capture; however, minor but significant amounts of K may be released (Semmens and Martin; 1988). Previous investigators of agronomic use of CRR for ammonium capture have not quantitatively addressed this issue, but it is probably important in regard to providing Ca and K as plant nutrients. In addition, gypsum is precipitated by the interaction of calcium released from CRRs and the sulfate provided by $(\text{NH}_4)_2\text{SO}_4$ fertilizer (Desborough, 1989). This is likewise beneficial because it provides both sulfur and calcium for plant growth long after commercial ammonium sulfate fertilizer is dissolved.

NH_4^+ -exchanged CRR could be used as a soil amendment for slow release of NH_4^+ ; however, if a Ca- and K-rich CRR is ammonium-exchanged before application to cropland, some Ca and K removed by the NH_4^+ exchange may cause the CRR to capture dissolved Ca and K from the soil as NH_4^+ is released. This may temporarily deprive the plants of a source of Ca and K in addition to that in the soil. One alternative to separate application of dry ammonium sulfate and dry CRR to soils might be applying them together in ratios desirable for the appropriate NH_4^+ availability and retention of ammonium in CRR. Another possibility is treatment of Ca plus K-rich CRR with commercially available ammonium polyphosphate solutions to exchange NH_4^+ for Na, Mg, Ca, and K in clinoptilolite, and simultaneously precipitate phosphate within the CRR fragments. This would provide temporary isolation of both NH_4^+ and P in CRR.

A major advantage of having ammonium and phosphate together is that when nitrification occurs ammonium is converted to nitrate and two H^+ ions are released from NH_4^+ , this acidic condition promotes dissolution of phosphate precipitated in CRR to release phosphorous.

OCCURRENCES OF CALCIUM PLUS POTASSIUM-RICH CLINOPTILOLITE-RICH ROCKS IN THE WESTERN U.S.

Only some CRR deposits in the western U.S. have a low sodium (< 2.5 weight percent) content and a high concentration of calcium plus potassium (4.5 weight percent or more). Sheppard and Gude (1982, table 3) reported chemical data for CRRs from 16 deposits in the western U.S.; only four of these have a low sodium content and high contents of calcium plus potassium. Chemical data reported by Desborough (1994, table 1) for CRRs from 17 deposits in the western U.S. and southern British Columbia shows that six of these deposits have low sodium and high concentrations of calcium plus potassium. Samples from these six deposits were used for the present study; available chemical data for each are given in table 1. The dilutant minerals in them are listed in table 2.

Table 1. Concentrations of certain elements in raw clinoptilolite-rich rocks from the Western U.S. that have high concentrations of calcium plus potassium.

[n.a., not analyzed; n.r., not reported]

Locality and abbreviation	Na	K	Ca	Fe	Cu	Zn	Rb	Sr	Ba
	weight percent				-----parts per million-----				
<u>Colorado</u>									
Creede-CCO	n.a.	3.2	1.7	0.9	20	80	190	485	590
<u>Idaho</u>									
Crisman Hill-CHI	n.a.	4.1	1.0	1.5	60	110	200	155	735
Corp. reports	0.8	4.0	0.7	2.5	-----n.r.-----				
<u>Nevada</u>									
Fish Crk.-FCWN	n.a.	3.0	1.5	0.9	20	80	190	250	670
<u>New Mexico</u>									
St. Cloud-SNM	n.a.	1.9	2.7	0.9	20	70	40	1,700	1,030
Corp. reports	0.6	3.2	0.5	0.5	-----n.r.-----				
<u>Oregon</u>									
Sheaville-SVO	n.a.	4.1	1.0	1.8	20	90	160	190	1,190
Corp. reports									
<u>South Dakota</u>									
SDA	2.4	3.7	1.8	1.7	20	100	110	355	835

Table 2. Dilutant minerals in raw clinoptilolite-rich rocks from the western U.S. that have high concentrations of calcium plus potassium.

[Minerals are listed in order of decreasing abundance;
"clay" refers to layer silicates with a 10-angstrom spacing]

Locality and abbreviation	Dilutant minerals
<u>Colorado</u>	
Creede-CCO	opal, potassium feldspar (K-feldspar), plagioclase
<u>Idaho</u>	
Crisman Hill-CHI	opal, K-feldspar
<u>Nevada</u>	
Fish Crk.-FCWN	quartz, K-feldspar, plagioclase
<u>New Mexico</u>	
St. Cloud-SNM	opal, quartz, plagioclase, clay
<u>Oregon</u>	
Sheaville-SVO	clay, opal(?)
<u>South Dakota</u>	
SDA	quartz, calcite, plagioclase, K-feldspar, opal(?)

RATIONALE FOR LABORATORY INVESTIGATIONS

Studies of clinoptilolite-rich rocks (CRRs) from six deposits were conducted to examine and compare their intrinsic cation-exchange properties. This was done because recent studies of CRRs have shown that they have widely variable exchange properties in regard to cation preferences (Zamzow and others, 1989; Schultz and Zamzow, 1993; Vos and O'Hearn, 1993; Desborough, 1994; Desborough and Frishman, 1995). Prior to the studies of Franklin and others (1986) using synthetic zeolite of the faujasite structure, it was not realized that H^+ exchange (capture) was also significant during exchange in NH_4^+ -rich solutions; it was shown by them that the zeolite captured as much as 17 percent of H^+ during the displacement of Na^+ by NH_4^+ . Cation competition between H^+ and metals such as Cu and Zn in acidic and near-neutral drainages was only recently recognized (Desborough, 1994; Desborough and Frishman, 1995). Recent quantitative field studies of H^+ -preferring CRR versus another CRR have shown significant differences in H^+ capture between the two CRRs tested side-by-side in acidic (pH = 3.9) irrigation water (Desborough and Raymond, 1995). Such differences in H^+ affinity of CRRs will have implications regarding reactions in soils of different pH.

Because of the complex relations of cation exchange recognized in other studies of CRRs, it was decided that laboratory exchange studies should include exposure to common cations, as well as crop-

fertilizer additives. These exchanges included ammonium, phosphorous, calcium, potassium, acidic solutions, and near-neutral pH water in the absence of soil biota that are very important to soil, fertilizer, and soil amendment interactions that affect plant growth viability and productivity.

LABORATORY METHODS

Samples of clinoptilolite-rich rocks (CRRs) from six deposits in the western U.S. were each treated in side-by-side tests for comparative responses to high concentrations of common cation salts (Na, K, Ca, and NH_4^+), low concentrations of H^+ (pH = 2.1 and 2.8), and near-neutral pH water. This was done to measure their relative preferences for these cations, and the relative exchange capacities for some of the cations that are essential nutrients for plant growth. All treated samples were sized to 2.0-4.7 mm after crushing. Cation salt solutions used were: 25 weight percent NaCl, 24 weight percent KCl, 40 weight percent CaCl_2 , and 24 weight percent NH_4Cl . The weight/volume ratio of CRR:solution was 1:8 (e.g. 5 grams CRR to 40 ml of each exchange solution) for all serial exchanges. Up to five serial exchanges were done. Exchange periods ranged from about five to nine days. After each exchange the solution was removed and the samples were rinsed in 200 ml of 55° C tap water and dried for 12 to 15 hours at 55° C prior to the next exchange. If the samples were to be chemically analyzed, they were pulverized to 95 % <0.10 mm in tungsten-carbide-lined ball mills, leached with 200 ml of 55° C tap water to remove soluble salts, retained on filter paper, and dried at 55° C prior to analysis. Quantitative analysis for K and Ca were done using a Li-drifted Si detector on an energy dispersive x-ray analyzer with an Fe^{55} radioisotope source, and well-known standards. Two or three aliquots were analyzed for each sample; the mean of these is reported. Measurements of pH were done with a temperature-corrected digital meter that was calibrated at pH of 7 and 4, prior to each set of measurements. Quantitative analyses of N in solids and liquids was done by Huffman Laboratories, Inc., Golden, CO using the Dumont method.

RESULTS FOR SERIAL EXCHANGES

Set A. Twenty-five grams of 2.0-4.7 mm CRR samples were each immersed in 200 ml of acetic acid solution of pH = 2.1 for 143 hours. This was done to remove acid-soluble minerals such as calcite or other carbonates. After rinsing and drying, 5 grams of each sample was exposed to 40 ml of 25 percent NaCl solution for 241.5 hours. The pH of each solution was measured each day and the results are shown on figure 1; the final H^+ concentrations of the solutions differ as much as a factor of 100. These differences are attributed chiefly to differences in CRR affinities for sodium and hydrogen. After the NaCl exchange, the next exchange (AC) used 5 grams of CRR in 40 ml of acetic acid (pH = 2.8) the final pH of the solutions were similar for five of the CRRs but the solution with SVO was consistently, and significantly lower than the others

(fig. 2). After the acetic acid exchange, the next exchange (AE) used 5 grams of CRR in 40 ml of 24 weight percent of ammonium chloride solution for 145.7 hours; figure 3 shows that all CRRs responded similarly, except that SDA retained slightly more H^+ than the others. After the 24 percent ammonium chloride exchange the samples were analyzed to measure the net losses of K and Ca due to the multiple exchanges (table 3). The largest amounts of K were lost from CHI and SVO; SNM lost the most Ca.

Table 3. Amounts of potassium and calcium in clinoptilolite-rich rocks after 24 percent ammonium chloride exchange (AE), and amounts lost (-) due to exchanges. Two acetic acid and one NaCl exchange preceded the ammonium chloride exchange.

CRR	CCO	CHI	FCWN	SNM	SVO	SDA
-----weightpercent-----						
K	2.4	0.7	2.0	1.3	0.7	1.5
K lost	-0.8	-3.4	-1.0	-0.6	-3.4	-2.2
Ca	0.7	0.4	0.9	0.4	0.3	0.7
Ca lost	-1.0	-0.6	-0.6	-2.3	-0.7	-1.1

Set B. Twenty-five grams of each raw CRR were immersed in 200 ml of 25 percent NaCl solution of pH = 6.9 for 120 hours. The pH was not monitored during the first two days, because it was not expected to change. However, after 120 hours, the final pH of the solution containing SVO decreased to 3.3; the final pH of the other solutions was 5.6 to 6.6. This is examined later in other series of exchanges using longer dwell periods. The next exchange (BB) used 5 grams of CCR in 40 ml of acetic acid (pH = 2.8); the pH of the final solutions after 244 hours ranged from 3.1 to 4.4. The higher pH solutions were possibly caused by dissolution of calcite in the CRR fragments. Exchange BC used 25 percent NaCl solution of initial pH of 7.4 for 168 hours; this was the second NaCl exchange for these CRRs. Figure 4 is a plot of pH changes of the solution which was made acidic (pH = 2.8-4.7) due to displacement of H^+ by Na^+ . Differences in final H^+ concentrations of these solutions varied by more than an order of magnitude, as was observed in exchanges of Set A. SDA has significantly more affinity for H^+ than for Na^+ , as was previously shown. Exchange BD used acetic acid (pH = 2.8) under the same conditions as BB above for 145 hours. Changes in solution pH are on figure 5 which shows slight differences in the preferences of the CRRs for H^+ . The last exchange for this set was BG in which 5 grams of each CRR was exposed to 40 ml of 40 percent calcium chloride (pH = 5.7) for 213.7 hours. The pH values of the exchange solutions are plotted on figure 6; final values of solution pH range from 1.9 to 2.6.

The final solution pH value of 1.9 and 2.1 for CHI and CCO, respectively, shows their stronger preference for Ca^{+2} over H^{+} , compared to the other CRRs. Table 4 shows the amounts of potassium and calcium in the CRRs after the 40 percent calcium chloride exchange; it also shows the amounts of calcium gained after the exchange, and the amounts of potassium lost after all five exchanges.

Table 4. Amounts of potassium and calcium in clinoptilolite-rich rocks after 40 percent calcium chloride exchange (BG), and the amounts of calcium gained and the amounts of potassium lost (-).

CRR	CCO	CHI	FCWN	SNM	SVO	SDA
	-----weightpercent-----					
K	2.7	1.6	2.1	1.7	1.8	2.1
K lost	-0.5	-2.5	-0.9	-1.5	-2.3	-1.6
Ca	2.5	2.5	2.2	2.8	2.9	3.2
Ca gained	0.8	1.5	0.7	0.1	1.9	1.4

Set B1. This set was done to examine the affects of only sodium chloride exchange followed by acetic acid exchange. The first exchange used five grams of raw CRRs placed in 40 ml of 25 percent sodium chloride solution (pH = 6.9) for 119.4 hours. Figure 7 shows the changes in pH of the solutions; SVO severely depressed the pH of the sodium chloride solution to 3.3. Because this is observed repeatedly for this sample, in all of the sodium chloride solutions, it is inferred that some metal hydroxide might be forming. This may be the case, but no precipitate is visible in the exchange solution; it may be inside of and on the CRR fragments. The next exchange was BF for which 5 grams of each CRR was placed in 40 ml of acetic acid (pH = 2.8) for 215 hours. Values of final solution pH ranged from 3.7 to 4.8; the higher values may be due to calcite dissolution in SDA. The last exchange (BH) was also 5 grams of each CRR placed in 40 ml of acetic acid (pH = 2.8) for 192 hours. Figure 8 is a plot of solution pH versus time. All CRRs responded similarly in raising solution pH to 3.2 to 3.4. Table 5 shows the concentrations of potassium and calcium in the CRRs and the amounts of potassium and calcium lost after the second acetic acid exchange.

Table 5. Amounts of potassium and calcium in clinoptilolite-rich rocks, and amounts of potassium and calcium lost (-) after acetic acid exchange BH.

CRR	CCO	CHI	FCWN	SNM	SVO	SDA
	-----weight percent-----					
-						
K	2.9	2.3	2.6	1.1	2.6	2.6
K lost	-0.3	-1.8	-0.4	-0.8	-1.5	-1.1
Ca	0.9	0.5	1.1	2.7	0.6	1.3
Ca lost	-0.8	-0.5	-0.4	0	-0.4	-0.5

Set B2. This set had only two exchanges. The first was 5 grams of each CRR in 40 ml of 25 percent sodium chloride (pH = 7.0) for 185 hours to once again examine the pH relations of the solutions. Results are shown on figure 9 where SVO again severely depressed the pH of the sodium chloride solution. The next exchange (B2A) was 5 grams of each Na-exchanged CRR in 40 ml of 24 percent potassium chloride solution of pH = 7.6. The final pH of each solution (not shown) after 168 hours ranged from 5.7 to 7.8; the exchange solution of SVO had the lowest pH and the solution of SDA had the highest pH. Table 6 shows the concentration of potassium and calcium in the CRRs, and the amounts of potassium gained and the amounts of calcium lost after the 24 percent potassium chloride exchange which was preceded by NaCl exchange. The amount of exchangeable potassium capacity can be deduced by the amount of potassium remaining after the 24 weight percent ammonium chloride exchange (table 3), versus the amount of potassium after the 24 percent potassium chloride exchange (table 6). SVO and SDA have the greatest K-exchange capacities of 5.2 and 5.1 weight percent respectively; K-exchange capacities of the other four CRRs range from 3.2 to 4.4 weight percent.

Table 6. Amounts of potassium and calcium in clinoptilolite-rich rocks, and the amounts of potassium gained and amounts of calcium lost (-) after the 24 percent potassium chloride exchange (B2A).

CRR	CCO	CHI	FCWN	SNM	SVO	SDA
	-----weight percent-----					
K	5.6	5.0	5.7	5.7	5.9	6.6
K gained	2.9	0.9	2.7	3.8	0.9	2.9
Ca	0.6	0.5	1.0	0.6	0.5	1.7
Ca lost	-1.1	-0.5	-0.5	-2.1	-0.5	-0.1

Set C. The first exchange (C) was 5 grams of raw CRR in 40 ml of acetic acid of pH = 2.8 for 140 hours. Results (not shown) were similar to prior tests with final pH values in the range of 3.5 to 3.7, except for SDA which raised the pH to 4.5. The second exchange (CA) was 5 grams of each CRR in 40 ml of 25 percent sodium chloride solution of pH = 7.8 for 194 hours. Figure 10 shows the final H⁺ concentrations of the solutions differ by two orders of magnitude; SVO depressed the solution pH to 2.2, whereas SDA depressed the solution pH to only 4.3. The last exchange (CB) was 5 grams of each CRR in 40 ml of acetic acid (pH = 2.8) for 192 hours. The relations of solution pH are shown on Figure 11; CCO and SDA raised solution pH the most and SVO raised solution pH the smallest amount. The CRRs were analyzed for potassium and calcium after the last exchange; results are given in table 7.

Table 7. Amounts of potassium and calcium in clinoptilolite-rich rocks after acetic acid (pH = 2.8) exchange (CB), and the amounts of potassium and calcium lost (-) due to exchange.

CRR	CCO	CHI	FCWN	SNM	SVO	SDA
	-----weight percent-----					
K	2.9	2.4	2.6	1.6	2.6	2.4
K lost	-0.3	-1.7	-0.4	-0.3	-1.5	-1.3
Ca	0.7	0.5	0.8	0.9	0.5	0.5
Ca lost	-1.0	-0.5	-0.7	-1.8	-0.5	-1.4

REVIEW OF CATION-EXCHANGE RESULTS FOR SERIAL EXCHANGES

For the alternate acetic acid and 25 percent NaCl exchanges, SDA shows the least tendency to release H⁺ for Na⁺ capture, whereas SVO shows the greatest preference of Na⁺ over H⁺. This conclusion is based on the measurements of pH of the solutions during the exchanges (figs. 1, 2, 4, 5, 11). Exchanges in 25 percent NaCl solutions using raw CRRs resulted in minor to large depression of the pH of the exchange solutions; SVO depressed the solution pH about two orders of magnitude more than any other, and SDA depressed the solution pH the least (figs. 7, 9). The reason for this effect is not clear, but the results are repeatable. It was thought that the pH depression by SVO in NaCl solutions might be due to the interaction of chloride and SVO, but this effect was not observed in the 24 percent KCl exchanges with the CRRs.

CHI released the greatest amount of H⁺ to the solution during the 40 percent CaCl₂ exchange, showing a significantly greater preference for Ca⁺² over H⁺ than the other CRRs (fig. 6).

In order to assess the relative maximum amounts of K and Ca exchange capacities of the CRRs, the minimum amount of each of these elements remaining after 24 percent ammonium chloride (table

3) or acetic acid exchanges (table 7) was assumed to be non-exchangable. The difference in these minimum amounts was subtracted from the maximum amounts of K and Ca measured for the 24 percent KCl exchange (table 6), and the 40 percent CaCl₂ exchange (table 4), respectively. The results are given in table 8 which, for the conditions of these tests, shows that SVO and SDA have the greatest exchange capacities for K, and SNM, SVO, and SDA have the greatest exchange capacities for Ca.

Table 8. Relative maximum amounts of potassium and calcium exchange capacities determined in the present study.

CRR	CCO	CHI	FCWN	SNM	SVO	SDA
	-----weight percent-----					
K	3.2	4.3	3.7	4.4	5.2	5.1
Ca	1.8	2.1	1.4	2.4	2.6	2.5

INFLUENCE OF CLINOPTILOLITE-RICH ROCKS ON pH OF WATER

Five-gram samples of 2.0-4.7 mm CRR were each placed in 40 ml of neutral pH (7.0) tap water to determine their influence, if any, on pH. This was done in sealed plastic containers to avoid evaporation. Table 9 shows the results after 21 days for a CRR:water ratio of 1:8.

Table 9. Initial and final pH of tap water exposed to clinoptilolite-rich rocks for 21 days.

CRR	CCO	CHI	FCWN	SNM	SVO	SDA
initial pH	7.0	7.0	7.0	7.0	7.0	7.0
final pH	6.7	6.6	7.3	6.9	5.7	8.4

A similar experiment was done using 5 grams of each CRR in 15 ml of tap water of initial pH of 6.5 for 10 days; results are shown in Table 10. The data in Tables 9 and 10 show that four of the CRRs alter the pH of near-neutral tap water very little, if any. However, SVO reduces the pH by more than one unit, and SDA increases the pH by more than one unit. The increase of pH by SDA may be due to the presence of calcite. The decrease of pH caused by SVO is not understood. Orange-brown iron oxides up to 1 mm thick occur on large blocks of the SVO CRR; these are apparently joint fillings. A four-gram sample of SVO fragments with abundant iron oxides was placed in 32 ml of tap water of pH of 7.0 and sealed in a plastic container; after 30 days the pH of the water was 3.9 and remained at that value 13 days later.

Table 10. Initial and final pH of tap water exposed to clinoptilolite-rich rocks for 10 days.

CRR	CCO	CHI	FCWN	SNM	SVO	SDA
initial pH	6.5	6.5	6.5	6.5	6.5	6.5
final pH	6.5	6.6	7.4	7.1	5.4	8.4

Fragments of SVO that were completely free of iron stain were pulverized to powder. Five grams of SVO powder were exposed to 40 ml of tap water (pH = 7.6) in a sealed plastic container for 30 days; the final pH was 7.15, or essentially unchanged. In view of these results it must be concluded that the iron oxide in the SVO CRR must be causing the reduction in the pH of the near-neutral tap water. Five grams of SVO powder free of iron stain was placed in 40 ml of 25 weight percent NaCl solution of pH = 7.3; in 5.5 hours the solution pH was depressed to 5.2, and after 26 days the solution pH was 5.0. These results show that SVO is distinctly different from the other CRRs tested in relation to their influence on solution pH in 25 percent NaCl solutions. The reason for this effect is not clear.

CLINOPTILOLITE-RICH ROCKS REACTIONS WITH COMMERCIAL AMMONIUM FERTILIZER SOLUTIONS

Commercial liquid fertilizer composed of ammonium polyphosphate (10-34-0) approximately $(\text{NH}_4)_2\text{H}_3\text{P}_3\text{O}_{10}$ and ammonium nitrate (AN20) were used for evaluation of NH_4^+ uptake by CRRs. Because the ammonium polyphosphate liquid is very viscous (Specific Gravity = 1.43), it was diluted with three volumes of water; 10 grams of each CRR (2.0-4.7 mm granules) were placed in 30 ml of the diluted ammonium polyphosphate (Specific Gravity = 1.02) for 48 hours. After removal from the exchange solution each sample was dried at 55°C before grinding to powder. Four grams was removed for quantitative nitrogen analysis (Dumont method) and six grams was analyzed for K and Ca (Table 11).

Table 11. Concentrations of nitrogen, potassium, and calcium in ammonium polyphosphate-exchanged clinoptilolite-rich rocks. [N analyses by Huffman Laboratories, Inc., Golden, CO]

CRR	N	K	Ca
	-----weight percent-----		
CCO	2.9	2.4	1.0
CHI	2.7	1.9	0.6
FCWN	1.9	2.3	1.0
SNM	2.7	1.4	1.6
SVO	3.8	1.9	0.5
SDA	3.3	2.2	1.1

In order to evaluate the amounts of soluble salts left in the CRRs, four grams of each was leached with 100 ml of 55°C near-neutral tap water at rest for two hours. After leaching the powdered samples were retained on filter paper, dried at 55°C and weighed.

The weight percent of losses of this first leach are given in Table 12. One gram from each of these leached CRRs was then exposed to 900 ml of 22°C tap water at rest for one hour; the water was then decanted and 400 ml of tap water was exposed to each CRR at rest for an hour. After decanting the water, each CRR was exposed to an additional 400 ml of water at rest for 19 hours. The CRRs were retained on filter paper, dried at 55°C and weighed. The percent of weight lost for each during the second, third, and fourth leaches are given in Table 12. Cumulative weight lost due to removal of soluble salts ranges from 25 to 37 percent.

Table 12. Losses of water-soluble salts from ammonium polyphosphate-exchanged clinoptilolite-rich rocks exposed to near neutral water.

CRR	First leach	Second, third, and fourth leaches	
	4 g CRR in 100 ml, 55°C 2 hours	1 g CRR in 900, 400, and 400 ml, 22°C 1, 1, and 19 hours	
	-----weight percent lost-----		
			total--
CCO	23	11	34
CHI	29	8	37
FCWN	18	8	26
SNM	15	12	27
SVO	23	6	29
SDA	19	6	25

A second experiment was done with the ammonium polyphosphate (10-34-0) diluted in the same ratio (1:3) using 20 grams (2-4.7 mm) of each CRR in 60 ml of the liquid for 48 h. Afterward the "spent" liquid was drained from the CRRs which were dried at 55°C and weighed; the weight gained by the CRRs ranged from 2.2 to 7 percent. Ten grams of each CRR was pulverized and split for chemical analysis; one split was analyzed for total N, the other for Na, Mg, K and Ca. The results of these analyses are given in Table 13 which shows the amounts of N in CRRs differ by as much as 35 percent. The amounts of Na, Mg, K, Ca, and N in the CRRs after the exchanges includes both exchanged cations and "soluble salt" cations; the soluble cations remain in intracrystalline microscopic pore space of the CRRs.

Each spent liquid was filtered (0.8 micron) and the specific gravity of them ranged from 1.18 to 1.22; the specific gravity of the starting liquid was 1.02. Each spent liquid was split for analysis of NH_4^+ , and for Na, Mg, K, and Ca, respectively, and the results are given in Table 14. The amounts of dissolved Na, Mg, K, and Ca in the spent liquid can be used to calculate the amounts of N exchanged into the CRRs as NH_4^+ (Table 15). The non-exchanged

Table 13. Concentrations of Na, Mg, K, Ca, and N in clinoptilolite-rich rocks exposed to 1:3 diluted 10-34-0 ammonium polyphosphate liquid for 48 h. [Analysis of Na, Mg, K, and Ca were done by Actlabs, Inc., Wheat Ridge, CO; N analyses were done by Huffman Laboratories, Inc., Golden, CO]

CRR	Na	Mg	K	Ca	N
	-----weight percent-----				
CCO	0.60	0.38	2.52	0.94	2.57
CHI	0.25	0.12	2.07	0.46	2.53
FCWN	1.57	0.22	2.56	0.97	1.96
SNM	0.32	0.64	1.62	1.35	2.71
SVO	0.20	0.14	2.18	0.41	3.05
SDA	0.70	0.52	2.30	0.94	3.06
SDH495	0.67	0.46	2.30	0.85	3.05

or soluble N amounts given in Table 15 are the difference in the total N in the CRRs (Table 13) and the calculated-exchanged N. Differences in the amounts of exchanged N in the CRRs are greater than two-fold; differences in the amounts of water-soluble or non-exchanged N are more than four-fold (Table 15). The amounts of N remaining in the spent liquid are large, so that this spent liquid might be used as liquid fertilizer, or used for a second exposure to CRR, to make additional amended CRR for fertilizer use.

Table 14. Concentrations of Na, Mg, K, Ca, and N in spent liquids after exchange of clinoptilolite-rich rocks in 1:3 diluted 10-34-0 ammonium polyphosphate liquid for 48 h. [Analysis of Na, Mg, K, and Ca were done by Actlabs, Inc., Wheat Ridge, CO; N analyses were done by Huffman Laboratories, Inc., Golden, CO]

CRR liquid	Na	Mg	K	Ca	N
	----milligrams per liter-----				wt. %
CCO	1840	405	2900	2870	2.83
CHI	2150	335	8740	1530	2.97
FCWN	2900	437	3830	1940	2.52
SNM	957	661	1630	3010	2.97
SVO	3870	307	9120	1280	2.48
SDA	7160	322	4780	2480	2.00
SDH495	6540	309	4630	2480	2.44

Table 15. Amounts of nitrogen exchanged into clinoptilolite-rich rocks, and amounts of non-exchanged or water soluble nitrogen in clinoptilolite-rich rocks after exposure to 1:3 diluted 10-34-0 ammonium polyphosphate liquid for 48 h. [Exchanged nitrogen calculated from the amounts of Na, Mg, K, and Ca in spent liquid (Table 14). Water soluble or non-exchanged N obtained from difference in total N in CRRs and calculated exchanged N.]

CRR	Exchanged N (calculated)	Water soluble or non-exchanged N
	-----weight percent-----	
CCO	1.35	1.22
CHI	2.01	0.52
FCWN	1.52	0.44
SNM	1.00	1.71
SVO	2.39	0.66
SDA	2.70	0.36
SDH	2.55	0.50

Twenty-four grams of each CRR (2.0-4.7 mm dried at 55°C) were immersed for 48 h in 72 ml of 57.1 weight percent of reagent grade NH_4NO_3 solution of initial pH of 4.5. This solution is a standard liquid nitrogen fertilizer known in the fertilizer industry as AN20 (ammonium nitrate). The pH of each solution was measured during the 48 h exposure and the results are shown on Figure 12. Both CHI and SVO CRRs reduced the solution pH, whereas the other CRRs raised the pH of the solutions; SDA and FCWN nearly neutralized the pH of the exchange solution. The CRRs were removed from the solutions, drained, dried at 55°C, and weighed. Ten grams of each CRR was

pulverized and split for chemical analysis; one split was analyzed for total N, the other split was analyzed for Na, Mg, K, and Ca (Table 16). In addition, the percentages of weight gain of each CRR are shown in Table 16. The percentage of weight gain by the CRRs correlates ($r^2 = 96.4\%$) with the amounts of total N in the CRRs exposed to the AN20 solution. The amounts of N in the CRRs range from 4.7-8.2 weight percent (94 to 164 pounds of N per ton of CRR).

The spent exchange solutions were filtered (0.8 micron) and their specific gravities were determined to be no more than 2 percent greater than the initial specific gravity (1.25) of the AN20 solution. The concentrations of Na, Mg, K, and Ca in the spent AN20 liquids are given in Table 17; these represent the amounts of each of these cations displaced by exchange of NH_4^+ into the CRRs. In comparing the amounts of displaced cations (in spent solutions) in the 1:3 diluted 10-34-0 solutions (Table 14) with those of the spent solutions of AN20, the diluted 10-34-0 solutions caused more removal of Na and Mg, whereas AN20 solutions generally caused more exchange of K and Ca from the CRRs. The exception is the lower amounts of Ca removed from the SD CRRs by the acidic AN20 solution. Figure 13 shows that SDA raised the pH of the AN20 solution from 4.5 to about 6.5 in less than 48 h. This pH increase was initially thought to be due to dissolution of calcite in SDA. However, because much less Ca was present in the spent AN20 solution exposed to SDA (Table 17), than in the spent, near-neutral 1:3 diluted 10-34-0 solution (Table 14), calcite dissolution cannot be the reason. Instead, the stronger H^+ affinity of the SDA clinoptilolite is the reason for the large increase of the pH of the AN20 solution, as compared to the pH of the other AN20 solutions exposed to the other CRRs.

Table 16. Concentrations of Na, Mg, K, Ca, and N in clinoptilolite-rich rocks exposed to 57.1 weight percent of ammonium nitrate (AN20) for 48h. Weight gains are also given. [Analysis of Na, Mg, K, and Ca were done by Actlabs, Inc., Wheat Ridge, CO; N analysis were done by Huffmann Laboratories, Inc., Golden, CO]

CRR	Na	Mg	K	Ca	N	weight gain percent
	-----weight percent-----					
CCO-AN20	0.53	0.34	1.99	0.53	6.55	12.9
CHI-AN20	0.22	0.10	0.91	0.28	6.58	10.9
FCWN-AN20	1.47	0.21	1.96	0.82	4.71	6.3
SNM-AN20	0.28	0.57	1.25	0.82	6.50	12.2
SVO-AN20	0.16	0.12	0.79	0.32	8.07	16.5
SDA-AN20	0.61	0.44	1.45	1.23	8.20	16.4
SDH-AN20	0.57	0.41	1.49	1.08	8.17	15.9

Table 17. Concentrations of Na, Mg, K, and Ca in spent liquids after exchange of clinoptilolite-rich rocks in 57.1 weight percent of ammonium nitrate (AN20) for 48 h. [Analyses of Na, Mg, K, and Ca were done by Actlabs, Inc., Wheat Ridge, CO]

CRR liquid	Na	Mg	K	Ca
	-----milligrams per liter-----			
CCO-AN20	1400	174	4050	4340
CHI-AN20	1720	51	12200	1990
FCWN-AN20	2430	156	4720	2150
SNM-AN20	466	537	1840	4800
SVO-AN20	3120	22	12700	1430
SDA-AN20	6110	29	6200	1210
SDH-AN20	5540	21	6260	1390

Table 18 gives the amounts of N exchanged into the CRRs, and the amounts of water-soluble N in the pore space in each CRR after exposure to AN20 solutions for 48 h. Only about 12 to 25 percent of the total N in the CRRs is exchanged--the rest is water soluble and it is presumably present as water-soluble nitrate compounds within the CRR fragments.

Table 18. Amounts of nitrogen exchanged into clinoptilolite-rich rocks, and amounts of non-exchanged or water soluble nitrogen in clinoptilolite-rich rocks after exposure to 57.1 weight percent of ammonium nitrate (AN20) for 48 h. [Exchanged nitrogen calculated from the amounts of Na, Mg, K, and Ca in spent liquid (Table 17). Water soluble or non-exchanged N obtained from differences in total N in CRRs and calculated exchanged N.]

CRR	Exchanged N (calculated)	Water soluble or non-exchanged N
	-----weight percent-----	
CCO	1.15	5.40
CHI	1.85	4.73
FCWN	1.15	3.56
SNM	0.80	5.70
SVO	2.07	6.00
SDA	1.92	6.28
SDH	1.86	6.31

The amounts of cation-exchanged N as NH_4^+ in the CRRs exposed to the 1:3 diluted ammonium polyphosphate (10-34-0) solution (which contains about 3 weight percent of N as NH_4^+) are 12 to 17 percent greater than those of the CRRs exposed to the AN20 solution which

contained about 10 weight percent of N as NH_4^+ . These results may indicate that anionic species and anionic concentrations, or both, may affect NH_4^+ exchange by the CRRs.

CATION COMPETITION BETWEEN H^+ AND COMMON SOIL CATIONS IN SOLUTIONS

Chloride solutions containing high concentrations of Na, Mg, K, Ca, and NH_4^+ and a pH of about 4.2 to 4.3 (by adding acetic acid) were prepared in four different concentrations. One solution contained 663 mg/L of each of the cations, a second contained 331 mg/L of each cation, a third contained 133 mg/L of each cation, and a fourth contained 66 mg/L of each cation. Each 2.0-4.7 mm sample of each CRR was placed in one of each of these solutions in a CRR:solution ratio of 1:8. The pH of each solution was measured during exposure periods of 287 to 335 hours. This was done to examine the competition between H^+ and the other cations because it is important that soil pH be kept near neutral for optimum growth for most plants. Table 19 shows the results and gives the initial and final pH for each solution for each CRR and the exposure times. These data show that at high concentrations of cations in solution, CHI and SVO have less preference for H^+ than do the other CRRs. The lowest concentration of cations--66 mg/L, would be a most reasonable concentration for fertilized soil; at these concentrations, only SVO fails to bring the solution pH above 6.5.

Table 19. Initial and final pH of cation-rich acidic solutions to which clinoptilolite-rich rocks were exposed.
CRR:solution = 1:8 and exposure periods are given.

CRR	CCO	CHI	FCWN	SNM	SVO	SDA
663 mg/L of Na, Mg, K, Ca, and NH_4^+ , initial pH = 4.22						
final pH	6.35	5.92	7.32	7.16	4.34	7.72
335 hours						
331 mg/L of Na, Mg, K, Ca, and NH_4^+ , initial pH = 4.28						
final pH	6.33	5.81	7.43	6.94	4.51	7.90
312 hours						
133 mg/L of Na, Mg, K, Ca, and NH_4^+ , initial pH = 4.32						
final pH	6.61	6.28	7.81	7.29	4.96	8.67
310 hours						
66 mg/L of Na, Mg, K, Ca, and NH_4^+ , initial pH = 4.33						
final pH	6.53	6.54	8.00	7.39	5.36	8.78
287 hours						

SUMMARY

The most important result of these studies is the recognition that the six clinoptilolite-rich rocks from each of six deposits in the western U.S. vary widely in their reactions to chemical solutions, even though all of them are dominantly the mineral clinoptilolite, according to their X-ray diffraction patterns. Such significant differences among these CRRs have been demonstrated in side-by-side tests. The large differences in their NH_4^+ -exchange capacities in N-rich liquid fertilizer solutions is rather remarkable.

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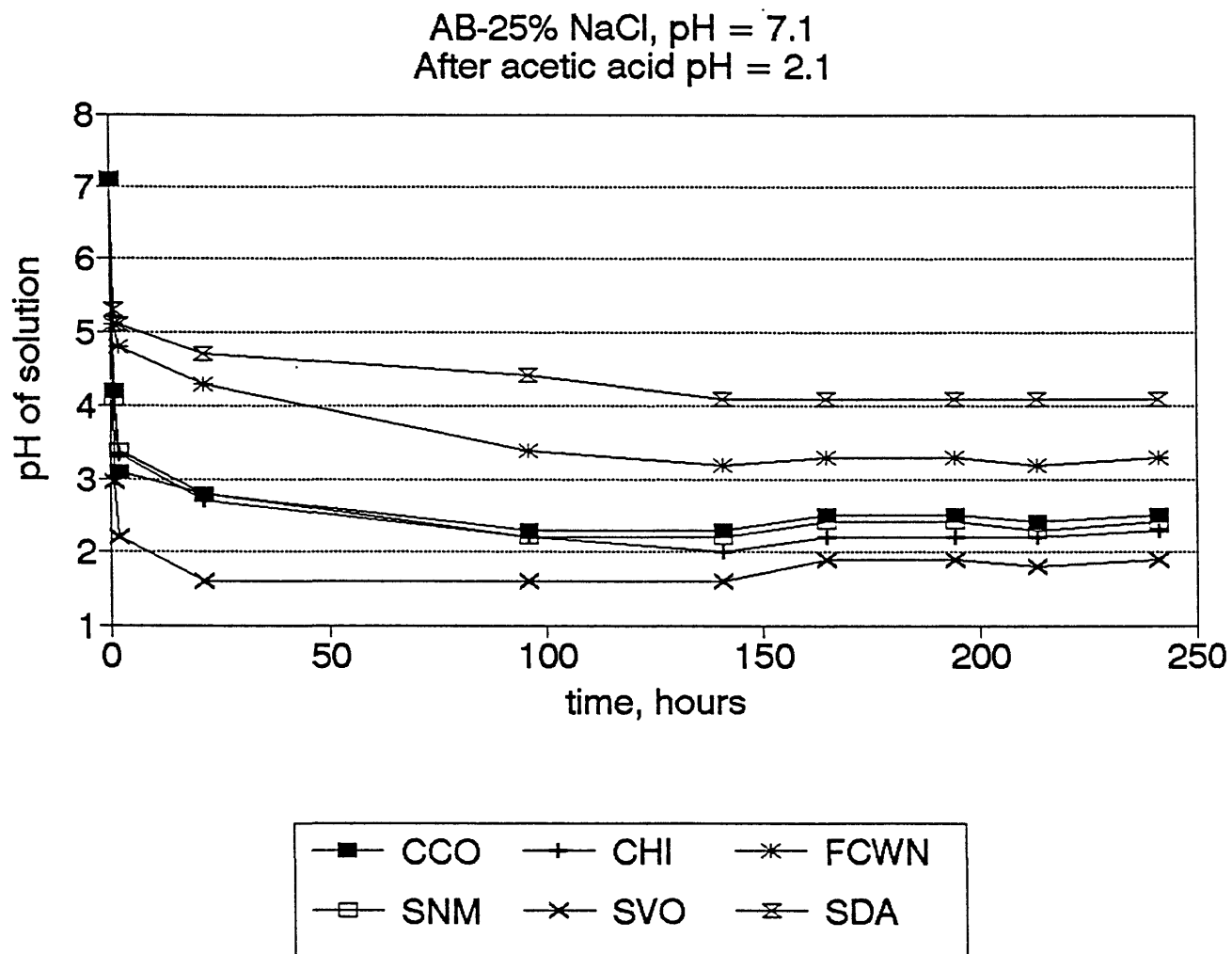


Figure 1. Relations of solution pH for clinoptilolite-rich rocks for exchange AB, 25 percent NaCl. (Abbreviations are defined on Table 1.)

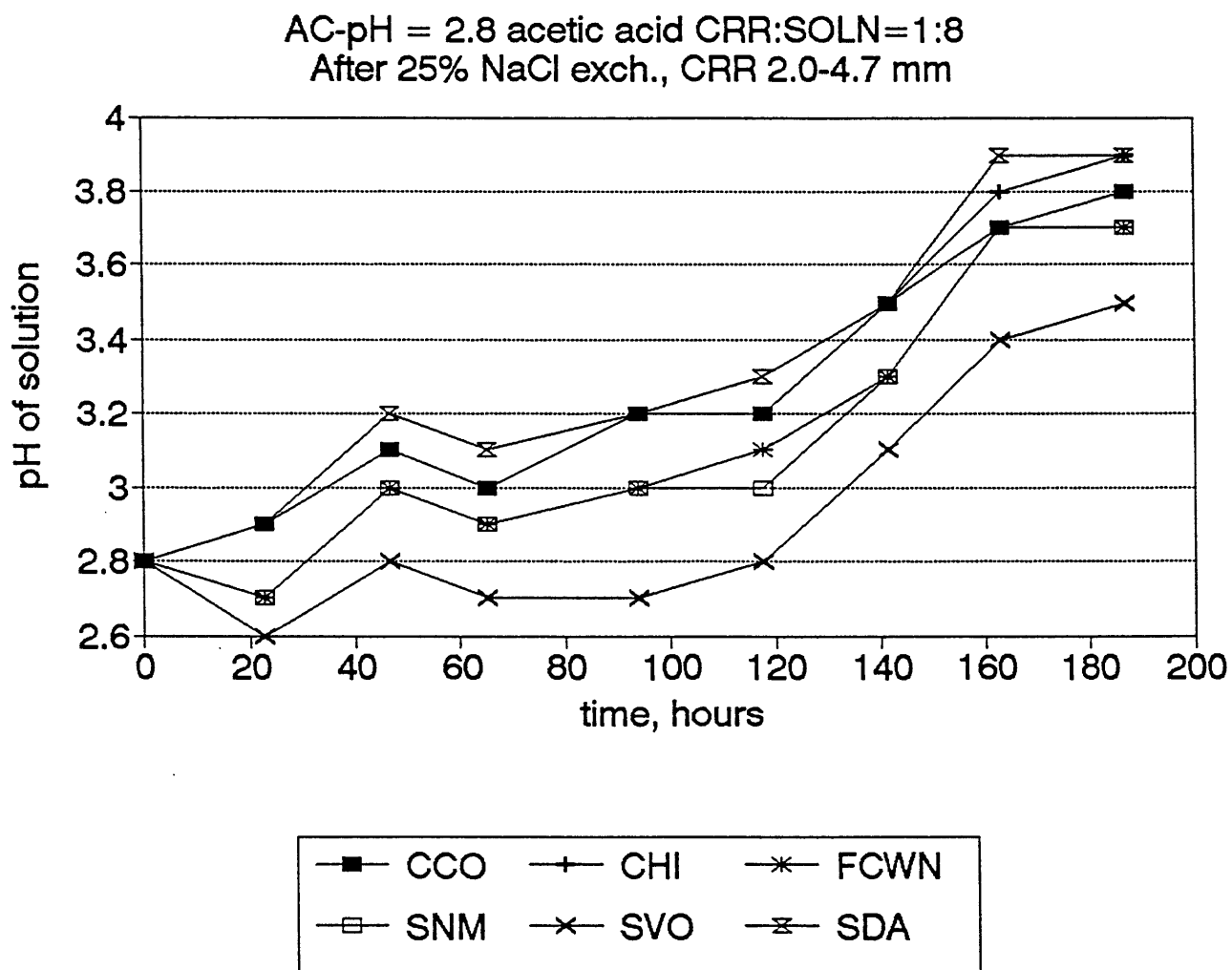


Figure 2. Relations of solution pH for clinoptilolite-rich rocks for exchange AC, acetic acid of pH 2.8, after 25 % NaCl exchange. (Abbreviations defined in Table 1.)

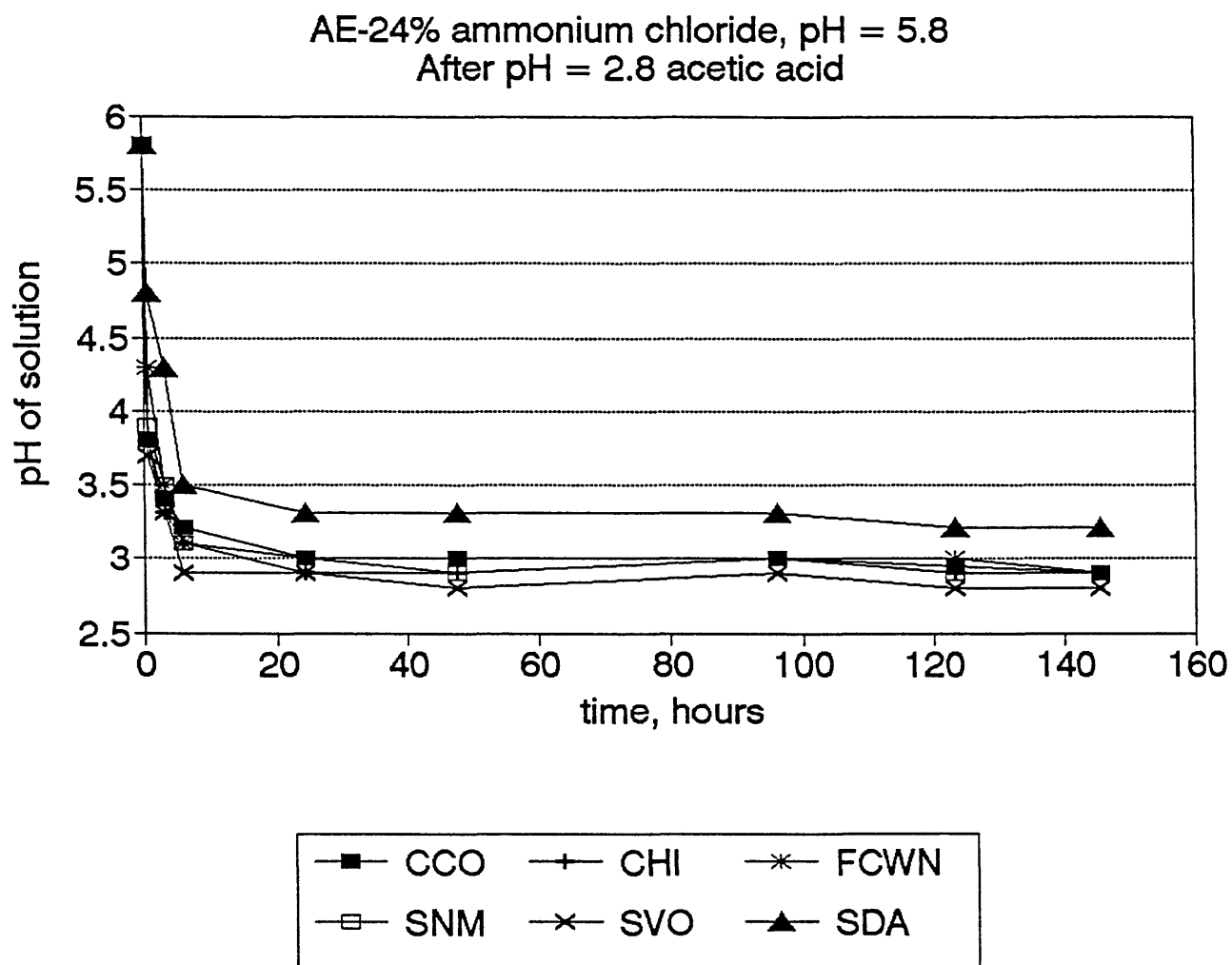


Figure 3. Relations of solution pH for clinoptilolite-rich rocks for exchange AE, 24 percent ammonium chloride, after pH = 2.8 acetic acid. (Abbreviations defined on Table 1).

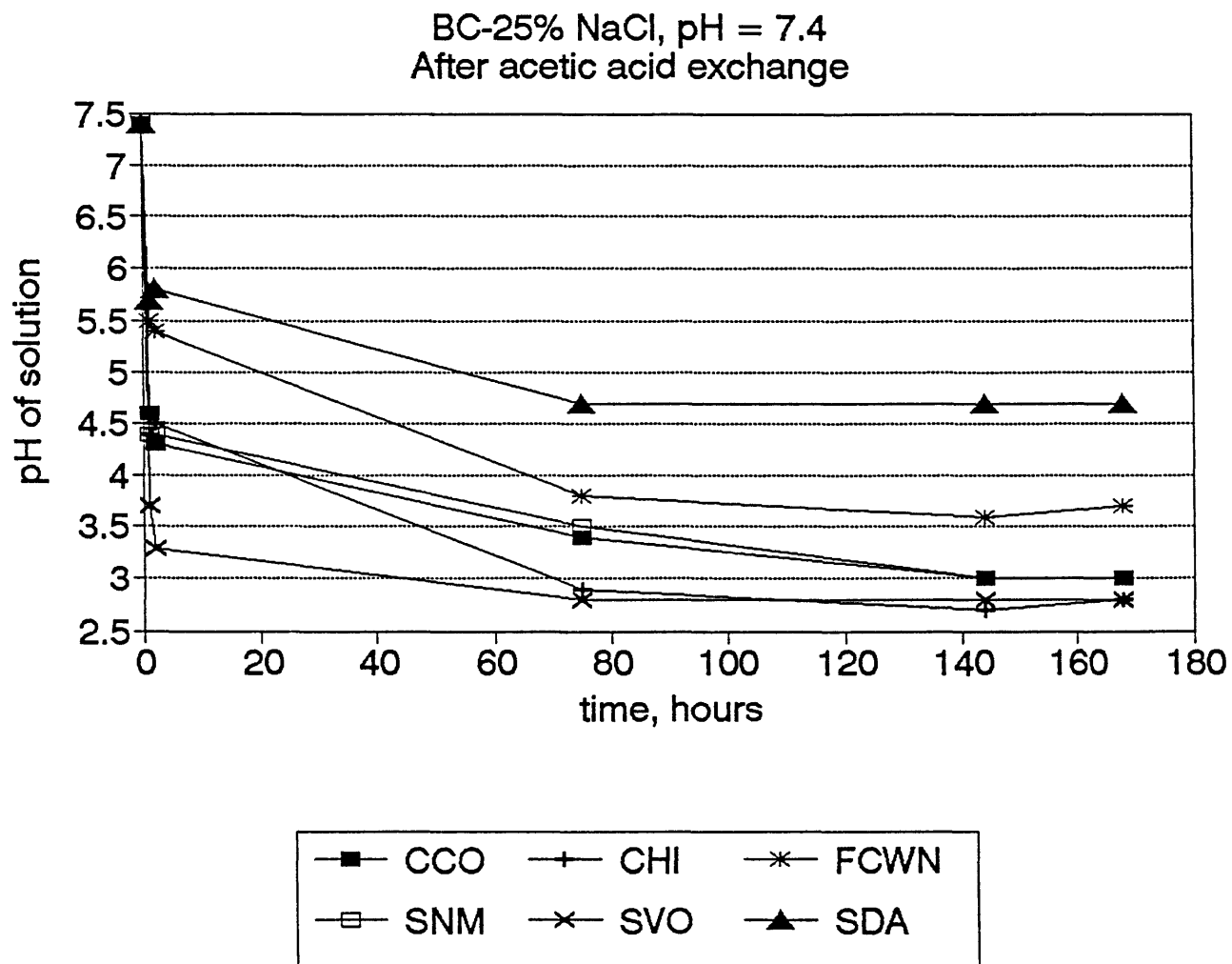


Figure 4. Relations of solution pH for clinoptilolite-rich rocks for exchange BC, 25 percent NaCl, after acetic acid exchange. (Abbreviations defined on Table 1.)

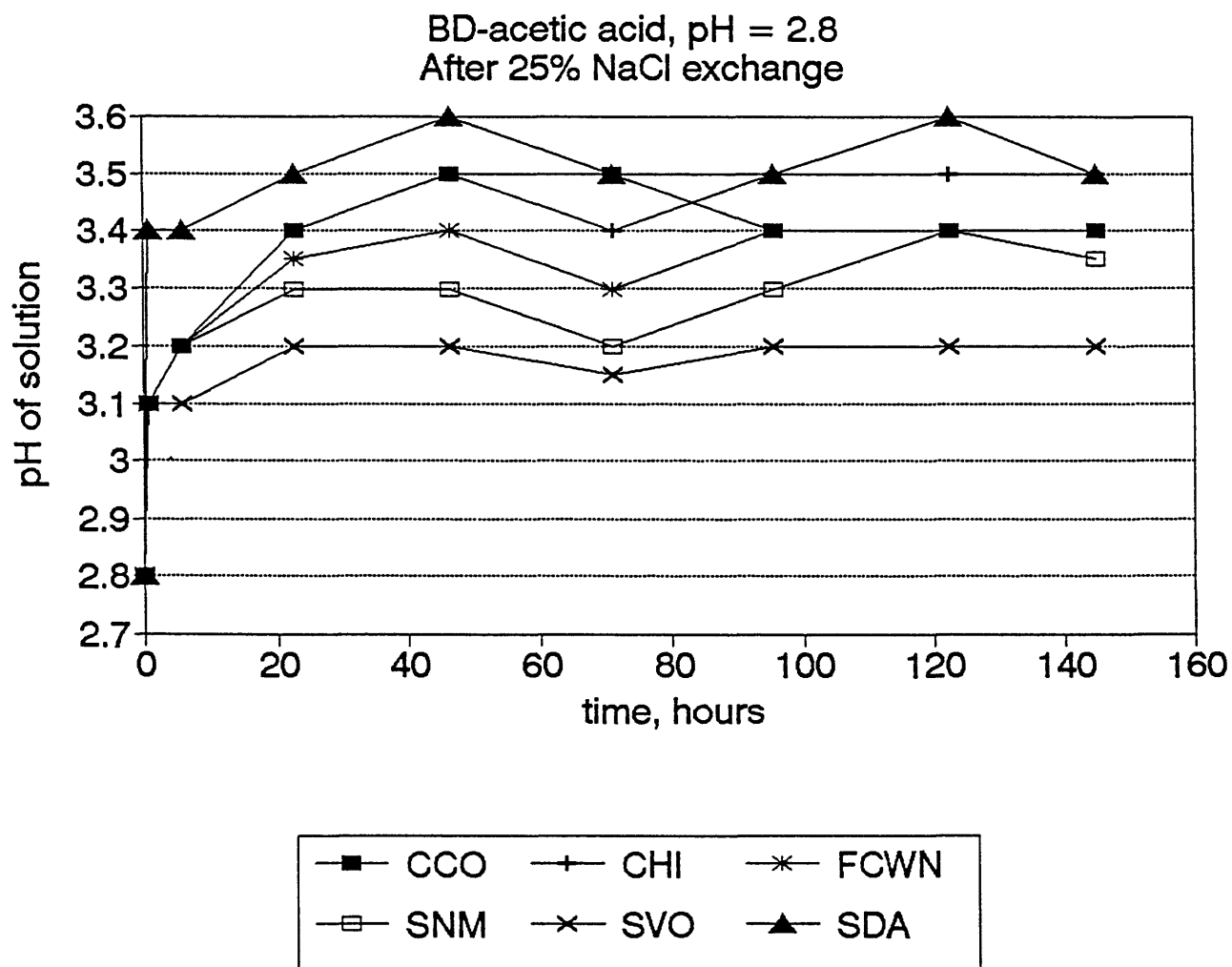


Figure 5. Relations of solution pH for clinoptilolite-rich rocks for exchange BD, acetic acid of pH = 2.8, after 25 % NaCl exchange. (Abbreviations are defined in Table 1.)

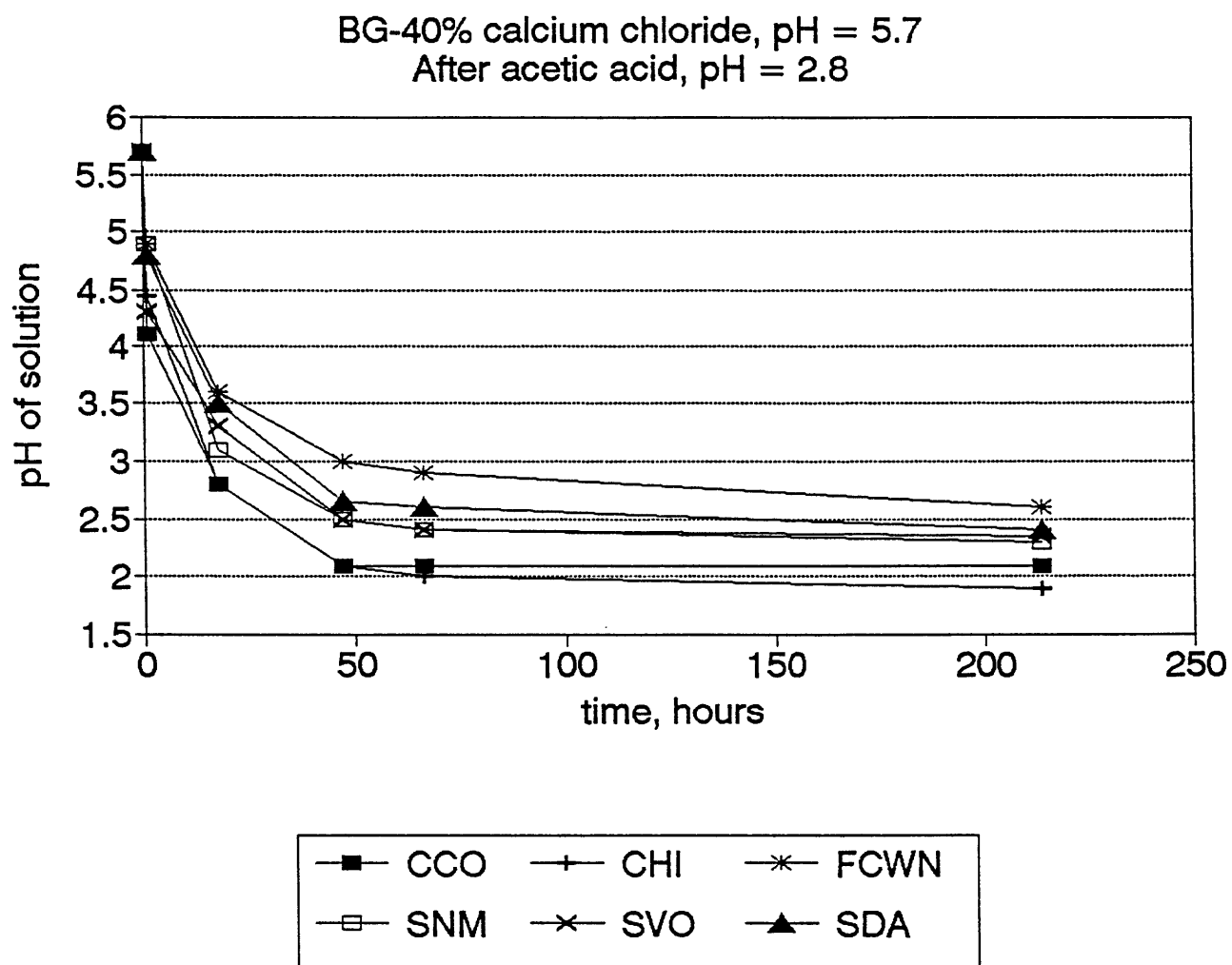


Figure 6. Relations of solution pH for clinoptilolite-rich rocks for exchange BG, 40 percent calcium chloride, after acetic acid exchange. (Abbreviations are defined in Table 1.)

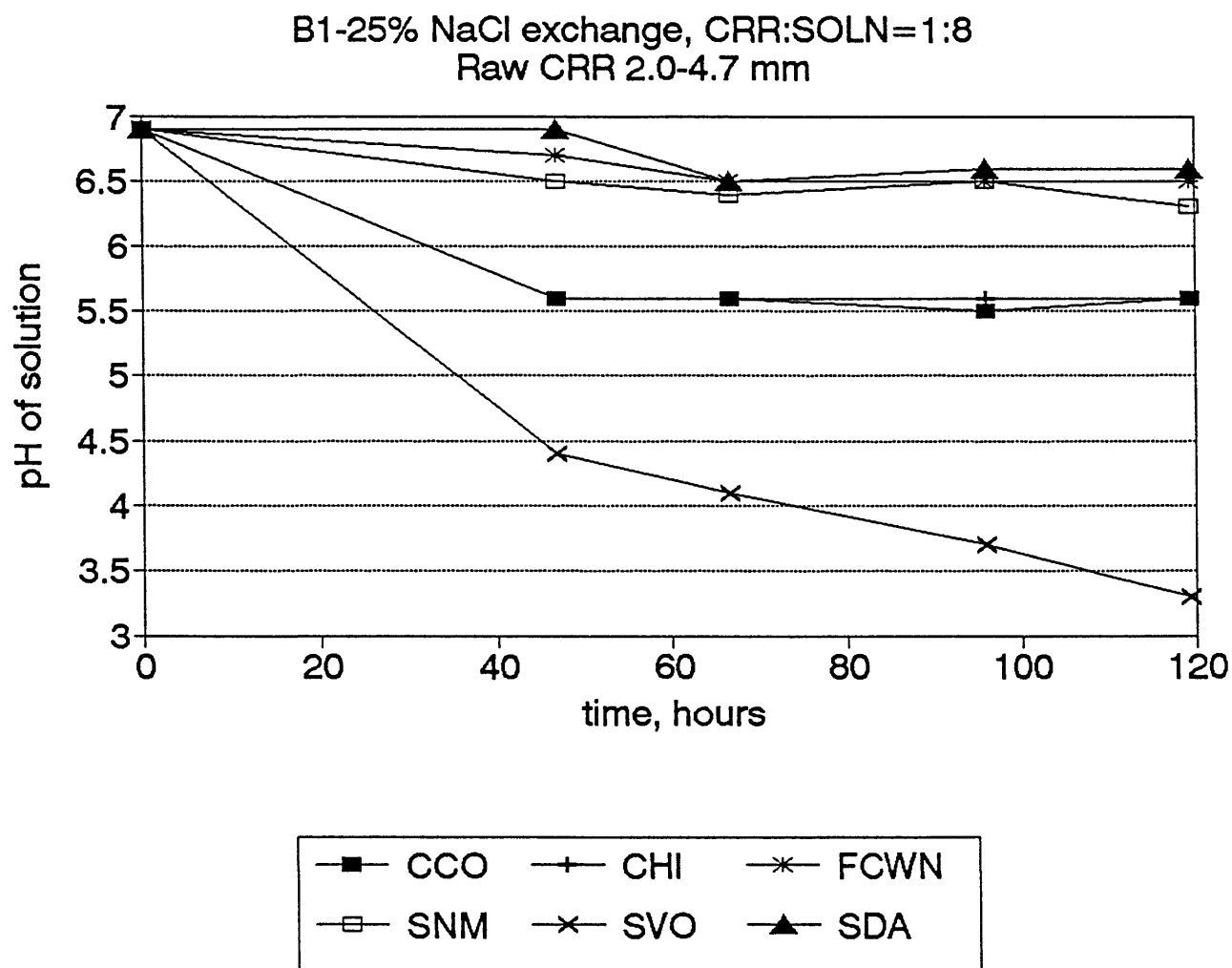


Figure 7. Relations of solution pH for clinoptilolite-rich rocks for exchange B1, 25 percent NaCl. (Abbreviations are defined in Table 1.)

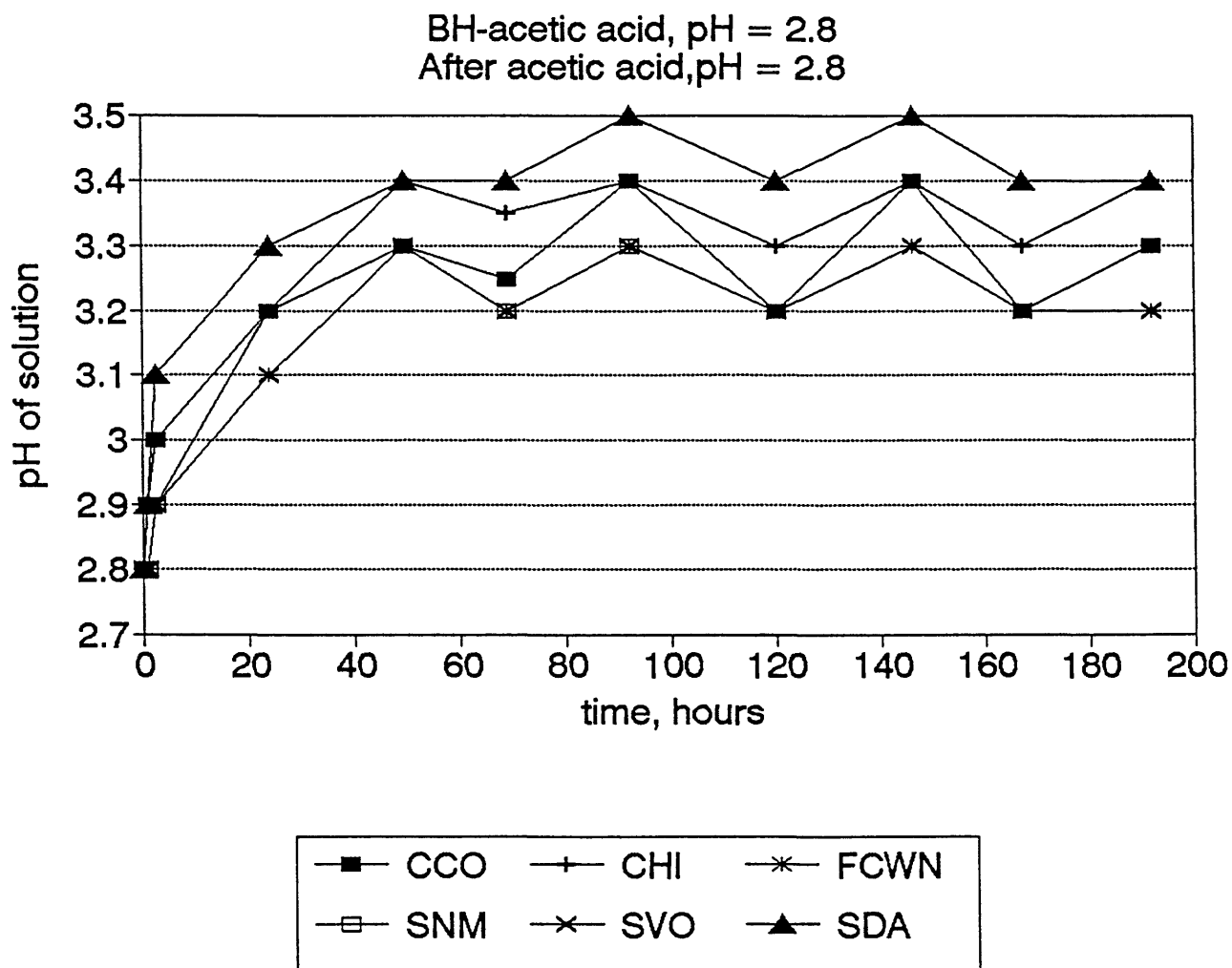


Figure 8. Relations of solution pH for clinoptilolite-rich rocks for exchange BH, acetic acid of pH = 2.8. (Abbreviations are defined in Table 1.)

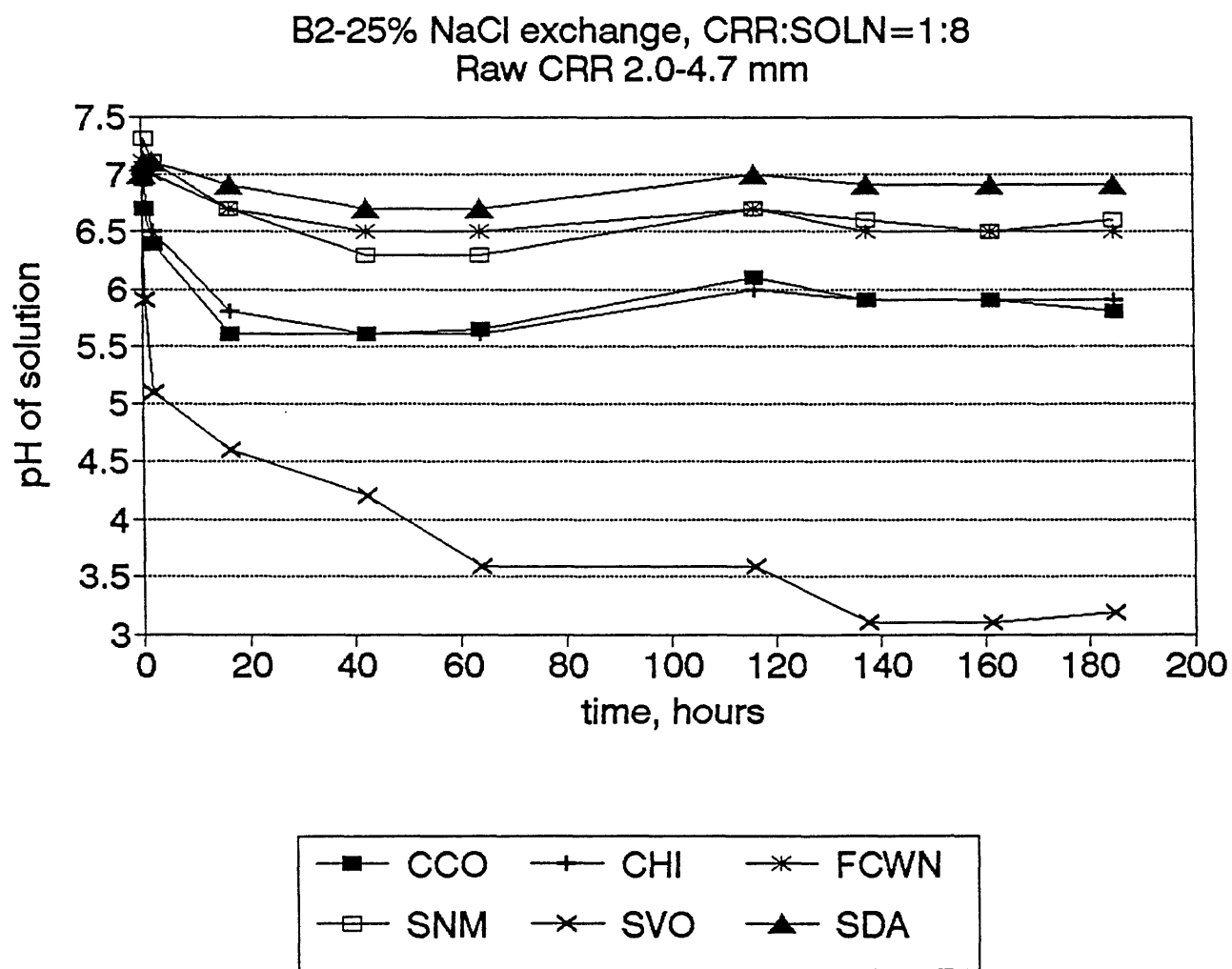


Figure 9. Relations of solution pH for clinoptilolite-rich rocks for exchange B2, 25 percent NaCl. (Abbreviations are defined in Table 1.)

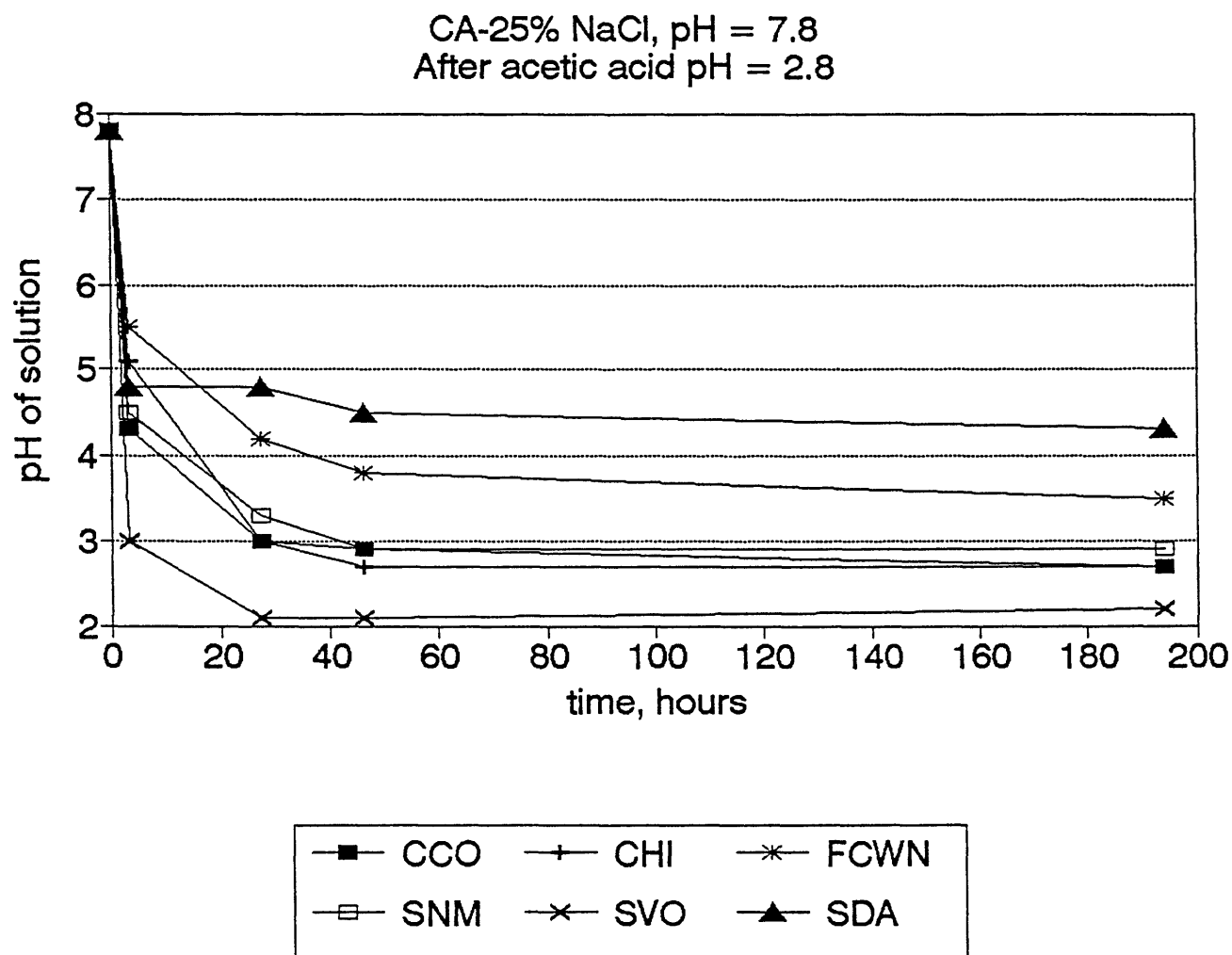


Figure 10. Relations of solution pH for clinoptilite-rich rocks for exchange CA, 25 percent NaCl, after acetic acid exchange. (Abbreviations are defined in Table 1.)

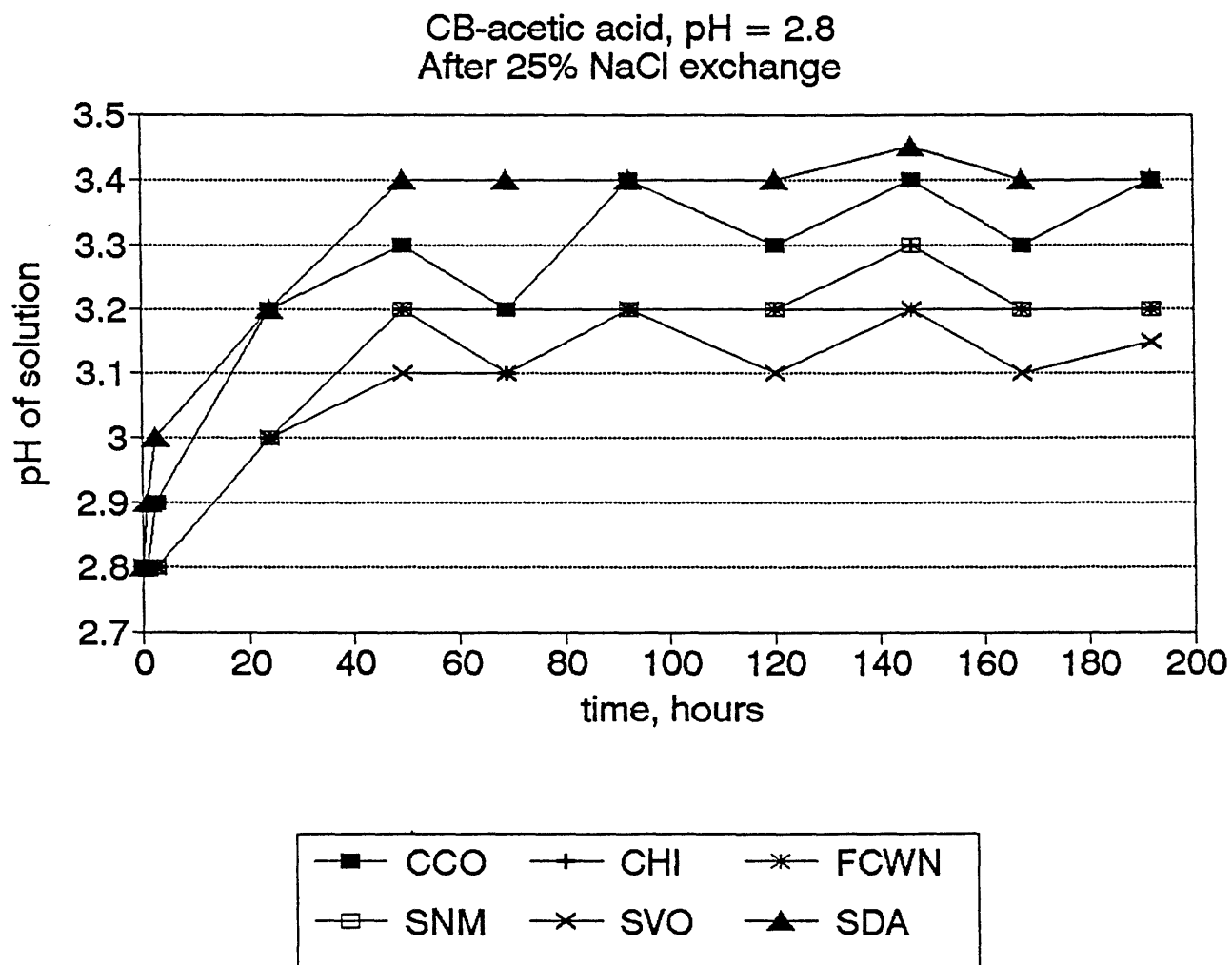


Figure 11. Relations of solution pH for clinoptilolite-rich rocks for exchange CB, acetic acid of pH = 2.8, after 25 % NaCl exchange. (Abbreviations are defined in Table 1.)

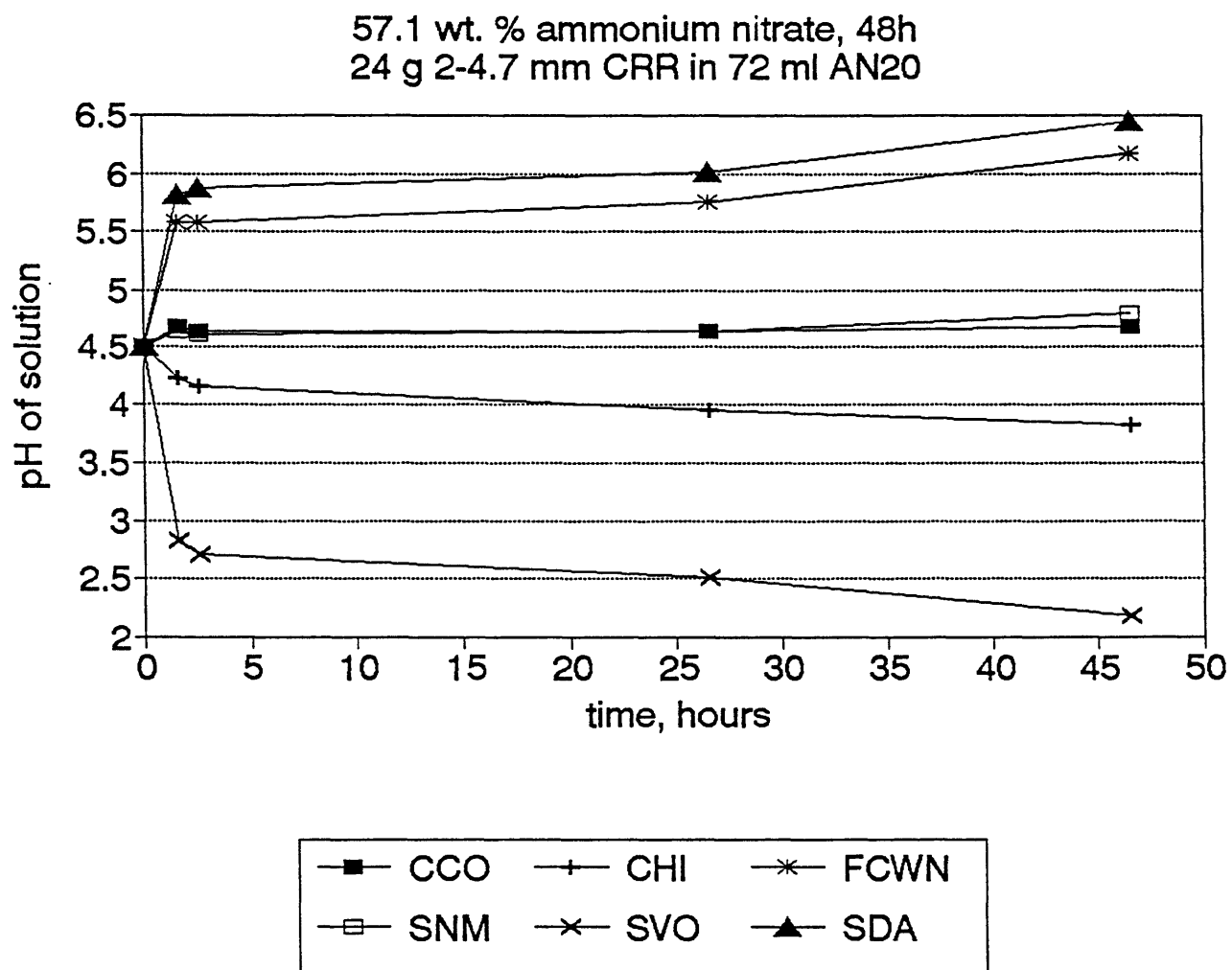


Figure 12. Relations of solution pH of 57.1 weight percent ammonium nitrate during immersion of clinoptilolite-rich rocks for 48 hours. (Abbreviations are defined in Table 1.)